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*THE DEVELOPMENT AND APPLICATION OF A GENERAL
EQUATION FOR FREE ENERGY AND
PHYSICO-CHEMICAL EQUILIBRIUM.*

BY GILBERT NEWTON LEWIS.

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INTRODUCTION.

THE advance of modern physical chemistry has been largely due to the application to physico-chemical problems of the first and second laws of thermodynamics and the gas law, — the latter both directly and by analogy. Upon this basis the whole theoretical treatment of chemical equilibrium rests at present. For this reason it may not be without interest to attempt to express the relations deduced from these laws in a single equation, the most convenient and the most general possible, which may serve to systematize a part of our present knowledge, and perhaps point out new laws. Such an attempt will be made in this paper.

I. GENERAL EQUATIONS OF FREE ENERGY AND EQUILIBRIUM.

The simplest expression embodying the first and second laws of thermodynamics is,

$$A = T \frac{dA}{dT} + U, \quad (1)$$

where A is the diminution in free energy (Helmholtz) of a system in any isothermal process; U is the diminution in internal energy in the same process; T is the absolute temperature; $\frac{dA}{dT}$ represents the change in A as the temperature of the process varies, — the system changing in every case from the same initial to the same final volume.

A , the diminution of free energy, is a quantity which denotes the maximum amount of work obtainable in an isothermal process, and which is determined definitely by the initial and final states of a system. It may,

therefore, be expressed as the difference between two quantities, one representing what may be called the total free energy of the initial state; the other, the total free energy of the final state. Representing these quantities by \mathfrak{A}_1 and \mathfrak{A}_2 , we have,

$$A = \mathfrak{A}_1 - \mathfrak{A}_2.$$

Similarly, if we represent by \mathfrak{U}_1 the total internal energy of the system in the initial state, and by \mathfrak{U}_2 the same in the final state,

$$U = \mathfrak{U}_1 - \mathfrak{U}_2,$$

equation (1) may be written,

$$\mathfrak{A}_1 - \mathfrak{A}_2 = T \frac{d\mathfrak{A}_1}{dT} - T \frac{d\mathfrak{A}_2}{dT} + \mathfrak{U}_1 - \mathfrak{U}_2,$$

$\frac{d\mathfrak{A}_1}{dT}$ and $\frac{d\mathfrak{A}_2}{dT}$ being taken at constant volume.

This equation may be separated into two equations,

$$\mathfrak{A}_1 = T \frac{d\mathfrak{A}_1}{dT} + \mathfrak{U}_1 + M, \quad (2a)$$

and

$$\mathfrak{A}_2 = T \frac{d\mathfrak{A}_2}{dT} + \mathfrak{U}_2 + M, \quad (2b)$$

where M is an undeterminable quantity which can have only arbitrary physical significance, since we are in practice only concerned with changes of free energy at constant temperature, and in such changes M always disappears.

In two special cases, viz. the ideal gas and the dilute solution, the expression for the change in free energy has been found to assume a very simple form,

$$A = n R T \ln \frac{v_2}{v_1},$$

where n denotes the number of gram-molecules of the gas or solute; R , the gas constant; T , the absolute temperature; \ln , a natural logarithm; v_1 and v_2 respectively, the initial and final molecular volumes. Although the above expression gives a complete statement for the change in free energy only in the two special cases mentioned, still we are led by many considerations to believe that it forms an important factor in many other, if not all, free energy changes. Evidence on this point is offered by the fact that the above term is present in the general equations of equilibrium which have found experimental verification in the most

diverse systems. Moreover, we are led to the above expression for free energy change by the kinetic theory, the extended application of which to much more complicated cases than that of a perfect gas has already produced important results.

The term $n R T \ln \frac{v_2}{v_1}$ may be written in the form

$$- n R T \ln v_1 + n R T \ln v_2.$$

Then we may consider that the quantity $- n R T \ln v_1$ represents an essential part of the free energy of n gram-molecules of a simple substance in a given state, and similarly, $n R T \ln v_2$, a similar part of the free energy in another state, and we may write for the free energy of one gram-molecule of a simple substance the entirely arbitrary equation,

$$\mathfrak{A}_1 = - R T \ln v_1 + x_1,$$

where x_1 represents that part of the free energy not contained in the term $- R T \ln v_1$; differentiating this equation,

$$\frac{d \mathfrak{A}_1}{d T} = - R \ln v_1 + y_1, \quad (3)$$

where $y_1 = \frac{d x_1}{d T}$.

Now substituting in equation (2 a),

$$\mathfrak{A}_1 = - R T \ln v_1 + y_1 T + \mathfrak{U}_1 + M. \quad (4)$$

Differentiating this at constant volume,

$$\frac{d \mathfrak{A}_1}{d T} = - R \ln v_1 + y_1 + T \frac{d y_1}{d T} + \frac{d \mathfrak{U}_1}{d T} + \frac{d M}{d T}.$$

Comparing this with equation (3),

$$T \frac{d y_1}{d T} + \frac{d \mathfrak{U}_1}{d T} + \frac{d M}{d T} = 0; \quad \frac{d y_1}{d T} = - \frac{1}{T} \frac{d \mathfrak{U}_1}{d T} - \frac{1}{T} \frac{d M}{d T}.$$

Since \mathfrak{U}_1 in this case represents the internal energy of one gram-molecule, $\frac{d \mathfrak{U}_1}{d T}$ at constant volume will be equal to the molecular heat capacity, at constant volume, which may be designated by c_{v_1} . Therefore,

$$d y_1 = - \frac{c_{v_1}}{T} d T - \frac{d M}{T}.$$

Integrating,

$$y_1 = - \int_{T_0}^T \frac{c_{v1}}{T} dT - \int_{M_{T_0}}^{M_T} \frac{dM}{T} + \mathfrak{H}_1,$$

where \mathfrak{H}_1 is the integration constant whose value depends on the value chosen for T_0 as the lower limit of integration. Substituting in equation (4), we obtain for \mathfrak{A}_1 , the free energy, per gram-molecule, of a simple substance in any given state,

$$\mathfrak{A}_1 = -R T \ln v_1 - T \int_{T_0}^T \frac{c_{v1}}{T} dT + \mathfrak{H}_1 T + \mathfrak{U}_1 + N, \quad (5)$$

where

$$N = M - T \int_{M_{T_0}}^{M_T} \frac{dM}{T},$$

and N is, like M , a quantity which will vanish in any expression for the difference in free energy at constant temperature.

From this we may obtain an equation for the change of free energy in any process. In the most general case, a system composed of any number, m_1 , of different molecular constituents,* and any amount, n_1 , n'_1 , etc. gram-molecules of each constituent, undergoes any change, physical or chemical, arriving at a condition in which it is composed of m_2 molecular constituents, and n_2 , n'_2 , etc. gram-molecules of each constituent.

If \mathfrak{A}_1 , \mathfrak{A}'_1 , etc. represent the free energies per gram-molecule of the various simple molecular constituents, a total change in free energy will be given by the equation,

$$A = (n_1 \mathfrak{A}_1 + n'_1 \mathfrak{A}'_1 + \dots) - (n_2 \mathfrak{A}_2 + n'_2 \mathfrak{A}'_2 + \dots).$$

If we substitute for \mathfrak{A}_1 , \mathfrak{A}'_1 , etc., their values as in equation (5), the N terms will all vanish and the equation will become,

$$\begin{aligned} A = & -R T (n_1 \ln v_1 + n'_1 \ln v'_1 + \dots - n_2 \ln v_2 - n'_2 \ln v'_2 - \dots) \\ & - T \int_{T_0}^T \frac{n_1 c_{v1} + n'_1 c'_{v1} + \dots - n_2 c_{v2} - n'_2 c'_{v2} - \dots}{T} dT \\ & + T (n_1 \mathfrak{H}_1 + n'_1 \mathfrak{H}'_1 + \dots - n_2 \mathfrak{H}_2 - n'_2 \mathfrak{H}'_2 - \dots) + (n_1 \mathfrak{U}_1 \\ & + n'_1 \mathfrak{U}'_1 + \dots - n_2 \mathfrak{U}_2 - n'_2 \mathfrak{U}'_2 - \dots). \end{aligned}$$

* Molecular constituent is used to mean a single molecular species in a single phase. Thus two phases of the same molecular species are regarded as two constituents, as are two different molecular species in the same phase.

If we represent by C_v and C_v' the total heat capacity, when each constituent remains at constant volume, in the initial and final states respectively; by H the total change in the various functions denoted by $n_1 \mathfrak{H}_1$, $n_2 \mathfrak{H}_2$, etc.; by U the total change in the internal energy of the system, then the equation may be written,

$$A = R T \ln \frac{v_2^{n_2} v_2'^{n_2'} \dots}{v_1^{n_1} v_1'^{n_1'} \dots} - T \int_{T_0}^T \frac{C_v - C_v'}{T} dT + H T + U. \quad (6)$$

We have in this equation a *perfectly general expression for the change of free energy in any isothermal change, chemical or physical, in any system, whether homogeneous or heterogeneous*. The quantities contained in the equation are all capable of direct experimental determination with the exception of the quantity H , of which we only know that it is not a function of the temperature, since it enters as the difference between a number of integration constants each of which is independent of the temperature. The value of this function and the simple form that it assumes in many important cases of equilibrium will be considered later.

The form which equation (6) takes in the simple cases where all the molecular species participating in the reaction are gases and dilute solutions may be shown as follows.

Equation (5), applying to the free energy of one of the simple constituents of a system, is,

$$\mathfrak{A} = -R T \ln v - T \int_{T_0}^T \frac{c_v}{T} dT + \mathfrak{H} T + \mathfrak{U} + N,$$

differentiated with respect to volume, at constant temperature,

$$\frac{d\mathfrak{A}}{dv} = -\frac{RT}{v} - T \int_{T_0}^T \frac{dc_v}{dv} \frac{1}{T} dT + T \frac{d\mathfrak{H}}{dv} + \frac{d\mathfrak{U}}{dv}. \quad (7)$$

Since $d\mathfrak{A}$ represents the work accomplished in a reversible change, we may write

$$d\mathfrak{A} = -p dv,$$

where p denotes the gas pressure or the osmotic pressure, as the case may be. Then

$$-p = -\frac{RT}{v} - T \int_{T_0}^T \frac{1}{T} \frac{dc_v}{dv} dT + T \frac{d\mathfrak{H}}{dv} + \frac{d\mathfrak{U}}{dv}. \quad (8)$$

Now we know that in the case of perfect gases and dilute solutions the heat of free expansion and the heat of dilution respectively are zero.

Therefore $\frac{d\mathfrak{U}}{dv} = 0$; moreover, $\frac{dc_v}{dv} = 0$. This is experimentally proved in the case of gases, and may be shown in the case of solutions as follows.

$$\frac{dc_v}{dv} = \frac{d\frac{d\mathfrak{U}}{dT}}{dv} = \frac{d^2\mathfrak{U}}{dv dT} = \frac{d\frac{d\mathfrak{U}}{dv}}{dT}; \quad (9)$$

now,

$$\frac{d\mathfrak{U}}{dv} = 0; \quad \frac{d\frac{d\mathfrak{U}}{dv}}{dT} = 0; \quad \text{and} \quad \frac{dc_v}{dv} = 0.$$

Equation (8) becomes

$$-p = -\frac{RT}{v} + T\frac{d\mathfrak{H}}{dv}.$$

But since we know that $p = \frac{RT}{v}$ is the characteristic equation of the perfect gas and the dilute solution, $\frac{d\mathfrak{H}}{dv} = 0$.

In these two simple cases, therefore, we find that \mathfrak{U} , c_v , \mathfrak{H} , are all independent of the volume. If then, equation (6) is applied to a reaction between gases and dilute solutions, the quantities \mathfrak{U}_1 , c_{v1} , \mathfrak{H}_1 ; \mathfrak{U}_2 , c_{v2} , \mathfrak{H}_2 , etc. will not at any given temperature change with changing volume, and the quantities U , $C_{v1} - C_{v2}$, H , will be constant, however the initial and final volume conditions of the system are changed. For any one temperature equation (6) may be written,

$$A = RT \ln \frac{v_2^{n_2} v_2'^{n_2'} \dots}{v_1^{n_1} v_1'^{n_1'} \dots} + C \text{ (a constant)}. \quad (10)$$

This equation, moreover, obviously applies to any system which contains, besides gases and dilute solutions, any constituents participating in the reaction, whose molecular volume is not changed appreciably by a change in the conditions of volume or pressure in the system. Thus any solid phase of definite constitution in a heterogeneous system may be considered constant in its molecular volume, as well as in its functions \mathfrak{U} , C_v , \mathfrak{H} , when the pressure of the system is varied through limits not too wide.

Since equation (6) gives an expression for the change of free energy in any isothermal process, we may derive immediately a general equation for equilibrium in any system. Let us consider a system such as is ordinarily studied, upon which the only external force is a uniform pressure,

normal to the surface, and in which the effects of gravity, surface tension, etc. may be neglected.

A necessary and sufficient condition for equilibrium is, that any change in a system in equilibrium is reversible. In other words, the change in the free energy of the system must be equal to the external work.*

In the case under consideration the external work is the product of the external pressure, P , by the change, V , in the volume of the system. Therefore in equilibrium,

$$A = P V. \quad (11)$$

Let us consider a system, of any degree of complexity, which is capable of change. In general this change will consist in a loss by some constituents of the system, accompanied by a corresponding gain by others. Then according to equation (6),

$$A = R T \ln \frac{v_2^{n_2} v'_2{}^{n'_2} \dots}{v_1^{n_1} v'_1{}^{n'_1} \dots} - T \int_{T_0}^T \frac{C_{v_1} - C_{v_2}}{T} dT + H T + U,$$

where quantities with subscript 1 refer to the constituents which suffer loss; those with subscript 2, to those which gain, and n_1 , n'_1 , etc., and n_2 , n'_2 , etc. represent the number of gram-molecules of each constituent lost and gained respectively.

Combining equations (6) and (11) we have as the general equation of equilibrium,

$$P V = R T \ln \frac{v_2^{n_2} v'_2{}^{n'_2} \dots}{v_1^{n_1} v'_1{}^{n'_1} \dots} - T \int_{T_0}^T \frac{C_{v_1} - C_{v_2}}{T} dT + H T + U, \quad (11a)$$

where P is the external pressure and V is the total change in volume.

$$V = (n_2 v_2 + n'_2 v'_2 + \dots) - (n_1 v_1 + n'_1 v'_1 + \dots).$$

This equation (11a) expresses the equilibrium of the system in regard to the particular change in question. When a system is in perfect equilibrium there will be an equation of the above form for every change or reaction which can take place independently. These equations, however, will not all be independent. For example, if both liquid and gaseous acetic acid are composed of two kinds of molecules, namely, CH_3COOH and $(\text{CH}_3\text{COOH})_2$, then when acetic acid and its vapor are in equilib-

* Of course the change must not be great enough to disturb the condition of equilibrium. The following demonstration would be somewhat more rigorous if the infinitesimal notation were used.

rium, we have four equations of the type of (11 a); one referring to the equilibrium in the gaseous state of the reaction, $2\text{CH}_3\text{COOH} = (\text{CH}_3\text{COOH})_2$; another, referring to the same reaction in the liquid phase; a third, referring to the liquefaction or vaporization of the double molecules; the fourth, to the liquefaction or vaporization of the single molecules. Of these four equations three are independent.

* Returning to the discussion of the general equation of equilibrium, equation (11 a), it is interesting first to determine what form it will take when we limit the system considered to the conditions under which equation (10) was deduced, namely, that the reacting system shall include, besides gases and dilute solutions, only "condensed" phases of definite composition. Combining equations (10) and (11),

$$P V = R T \ln \frac{v_2^{n_2} v_2'^{n_2'} \dots}{v_1^{n_1} v_1'^{n_1'} \dots} + C.$$

Now V , the change of volume, is due in this case to the change in volume of the gaseous constituents, and will therefore, at constant temperature, be inversely proportional to P . Therefore $P V$ is a constant, and at constant temperature,

$$\ln \frac{v_2^{n_2} v_2'^{n_2'} \dots}{v_1^{n_1} v_1'^{n_1'} \dots} = C', \quad \text{and} \quad \frac{v_2^{n_2} v_2'^{n_2'} \dots}{v_1^{n_1} v_1'^{n_1'} \dots} = K \text{ (a constant).} \quad (12)$$

This equation is the familiar mass law of Guldberg and Waage, but it is also, since it is not restricted to homogeneous systems; the law of the constancy of the ratio of distribution among different phases. This includes the law of Henry.

That equation (12) does not represent a universally accurate law of nature is shown by comparison with equation (11 a); for it is only when

$$U, H, C_{v_1} - C_{v_2}, \text{ and } P V \text{ are constant that } \frac{v_2^{n_2} v_2'^{n_2'} \dots}{v_1^{n_1} v_1'^{n_1'} \dots} \text{ is constant.}$$

If this fraction for convenience is denoted by K , which may be called, instead of the equilibrium constant, the equilibrium ratio, then K is a function, not only of the temperature, but also of $U, H, C_{v_1}, C_{v_2}, P V$. The nature of this function may be shown from equation (11 a),

$$R T \ln K = P V - U + T \int_{T_0}^T \frac{C_{v_1} - C_{v_2}}{T} dT - H T; \quad (13)$$

$$\ln K = \frac{1}{R} \left(\frac{P V}{T} - \frac{U}{T} + \int_{T_0}^T \frac{C_{v_1} - C_{v_2}}{T} dT - H \right); \quad (14)$$

$$K = e^{\frac{1}{R} \left(\frac{PV}{T} - \frac{U}{T} + \int_{T_0}^T \frac{C_{v_1} - C_{v_2}}{T} dT - H \right)}, \quad (15)$$

in which e is the base of the natural system of logarithms.

From this general equation of equilibrium may be easily deduced the expression for the change of the conditions of equilibrium with change of temperature. In equation (14) let, for convenience,

$$\int_{T_0}^T \frac{C_{v_1} - C_{v_2}}{T} dT - H = F, \quad (16)$$

equation (14) differentiated with respect to temperature then becomes

$$\frac{d \ln K}{dT} = \frac{1}{R} \left[\frac{d \left(\frac{PV}{T} \right)}{dT} - \frac{1}{T} \frac{dU}{dT} + \frac{U}{T^2} + \frac{dF}{dT} \right]. \quad (17)$$

Now F is a function of T and also of $\ln K$, which is itself a function of T . According to the laws of partial derivatives,

$$\frac{dF}{dT} = \frac{\delta F}{\delta T} + \frac{\delta F}{\delta \ln K} \frac{d \ln K}{dT},$$

where δ signifies a partial differential. Since H is independent of the temperature, and

$$F = \int_{T_0}^T \frac{C_{v_1} - C_{v_2}}{T} dT - H,$$

then,

$$\frac{\delta F}{\delta T} = \frac{C_{v_1} - C_{v_2}}{T} = \frac{1}{T} \frac{dU}{dT}, \quad \text{for } C_{v_1} - C_{v_2} = \frac{dU}{dT}.$$

Therefore,

$$\frac{dF}{dT} = \frac{1}{T} \frac{dU}{dT} + \frac{\delta F}{\delta \ln K} \frac{d \ln K}{dT},$$

and equation (17) becomes

$$\frac{d \ln K}{dT} = \frac{1}{R} \left[\frac{d \left(\frac{PV}{T} \right)}{dT} - \frac{1}{T} \frac{dU}{dT} + \frac{U}{T^2} + \frac{1}{T} \frac{dU}{dT} + \frac{\delta F}{\delta \ln K} \frac{d \ln K}{dT} \right],$$

and by transposition

$$\frac{d \ln K}{dT} \left(1 - \frac{1}{R} \frac{\delta F}{\delta \ln K} \right) = \frac{1}{R} \left[\frac{d \left(\frac{PV}{T} \right)}{dT} + \frac{U}{T^2} \right] \quad (18)$$

If we consider the special case of a system whose volume is unchanged by the reaction to which the equilibrium equation refers, then $V = 0$, and

$$\frac{d \ln K}{dT} \left(1 - \frac{1}{R} \frac{\delta F}{\delta \ln K} \right) = \frac{U}{R T^2}. \quad (19)$$

F , since it is equal to $\int_{T_0}^T \frac{C_{v1} - C_{v2}}{T} dT - H$, was shown to be constant under the conditions which led to equations (10) and (12), when the conditions of equilibrium changed at constant temperature. In such cases, therefore, $\frac{\delta F}{\delta \ln K} = 0$, and the equation becomes

$$\frac{d \ln K}{dT} = \frac{U}{R T^2}. \quad (20)$$

This equation applies to both homogeneous and heterogeneous equilibrium. When applied to the former it is identical with the well known equation of van't Hoff, sometimes called the equation "isochore." This equation, however, has been used to express the change of equilibrium with the temperature, not merely in those systems in which the reaction causes no change in volume, but in general. That this use is justifiable in the cases for which equation (20) was developed may be readily shown. For, in systems subject to moderate pressure, the only considerable isothermal changes in volume are those of the gaseous phase. The volume of the gases is, at a given pressure and temperature, proportional to the total number of gram-molecules of the various gases present. If, during the reaction to which the equation refers, there is a change of n gram-molecules in the gaseous phase, then the total change in volume is,

$$V = \frac{n R T}{P}, \quad \text{or} \quad \frac{P V}{T} = n R.$$

In the case under discussion, where $\frac{\delta F}{\delta \ln K} = 0$, equation (18) may be written,

$$\frac{d \ln K}{dT} = \frac{1}{R} \left(\frac{d \left(\frac{P V}{T} \right)}{dT} + \frac{U}{T^2} \right).$$

Since $\frac{P V}{T} = n R$, a constant,

$$\frac{d \ln K}{dT} = \frac{U}{R T^2}.$$

Similarly, for any system in general in which the pressure is not very great, $d\left(\frac{PV}{T}\right)$ will be negligible, and, for a very close approximation, equation (18) becomes

$$\frac{d \ln K}{d T} \left(1 - \frac{1}{R} \frac{\delta F}{\delta \ln K}\right) = \frac{U}{R T^2}. \quad (21)$$

Comparing equations (20) and (21), we see that the conditions under which the above law of van't Hoff holds true are practically the same as those under which the equation "isotherm" of the mass law, equation (12), is true; namely, that F , and therefore $C_{v1} - C_{v2}$ and H are, at constant temperature, independent of the volume conditions of the system.

The various equations which have been here deduced from the general equations of free energy and equilibrium can be best studied further by their application to special cases of equilibrium, which we will proceed to discuss somewhat systematically.

II. APPLICATION TO MONOMOLECULAR SYSTEMS.

(A.) *Homogeneous Systems.*

1. *Gases.* — The simplest conceivable case of physico-chemical equilibrium is offered by a single molecular species in a single phase in equilibrium with the external pressure. For this case the equation of condition has already been found, — equation (8), namely,

$$p = \frac{R T}{v} + T \int_{T_0}^T \frac{1}{T} \frac{d c_v}{d v} d T - T \frac{d \mathfrak{H}}{d v} - \frac{d \mathfrak{U}}{d v}.$$

In the case of a perfect gas it has been shown that

$$\frac{d c_v}{d v} = 0; \quad \frac{d \mathfrak{H}}{d v} = 0; \quad \frac{d \mathfrak{U}}{d v} = 0; \quad \text{and} \quad p = \frac{R T}{v}. \quad (22)$$

The next case that deserves attention is that of a compressed gas. Here, also, the specific heat at constant volume is independent of the volume. This has been shown to be true up to pressures of several thousand atmospheres.* A recent work has questioned the absolute accuracy of this law. We will return to this point later. Meanwhile we may consider $\frac{d c_v}{d v} = 0$, and equation (8) then simplifies to

* Mallard and Le Chatelier, Wied.-Beibl., XIV. 364.

$$p = \frac{R T}{v} - T \frac{d \mathfrak{H}}{d v} - \frac{d \mathfrak{U}}{d v}. \quad (23)$$

From equation (9), since $\frac{a c_v}{d v} = 0$, $\frac{d \left(\frac{d \mathfrak{U}}{d v} \right)}{d T} = 0$, and therefore the term $\frac{d \mathfrak{U}}{d v}$ is independent of the temperature when c_v is independent of the volume. This term represents the heat developed in the free expansion of a gas, and shows that when the internal energy of a gas increases with increasing volume, — that is, when there is a cooling effect on free expansion, — the gas will have lower than normal pressure.

Since $\frac{d \mathfrak{H}}{d v}$ is a function of the volume alone, we may write equation (23) in the form,

$$p = \left(\frac{R}{v} - F(v) \right) T - \frac{d \mathfrak{U}}{d v}. \quad (24)$$

And since $\frac{d \mathfrak{U}}{d v}$ is not a function of the temperature, the equation of a gas at constant volume, the "isochore," is,

$$p = A T - B, \text{ where } A \text{ and } B \text{ are constants.} \quad (25)$$

This equation has been proved experimentally by Ramsay and Young.*

The values of $\frac{d \mathfrak{U}}{d v}$ for a few gases may be found from the porous plug experiments of Joule and Thomson. These experimenters determined directly, not $\frac{d \mathfrak{U}}{d v}$, but $\frac{d \mathfrak{U}}{d p}$, and found that in all their experiments with a variety of gases and mixtures of gases that the latter quantity was independent of the actual pressure of the experiment. That is, at constant temperature $\frac{d \mathfrak{U}}{d p}$ is a constant. We may write

$$d v = - \frac{v^2}{R T} d p$$

from the gas law, neglecting the errors introduced by the deviations from this law, which are of much smaller order than the errors of the experimental results that we are using. Then,

* Zeit. Phys. Chem., I. 433.

$$\frac{d\mathfrak{U}}{dv} = -\frac{RT}{v^2} \frac{d\mathfrak{U}}{dp}. \quad (26)$$

We may now write for equation (24),

$$p = \left(\frac{R}{v} - F(v) \right) T + \frac{RT}{v^2} \frac{d\mathfrak{U}}{dp}.$$

Now, for reasons that will be obvious immediately, we will write with perfect generality in place of $\frac{R}{v} - F(v)$, $\frac{R}{v - f(v)}$, where $F(v)$ and $f(v)$ are different functions of v . Then,

$$p = \frac{RT}{v - f(v)} + \frac{RT}{v^2} \frac{d\mathfrak{U}}{dp}. \quad (27)$$

Now since the last term is independent of the temperature, $\frac{d\mathfrak{U}}{dp} RT$ must be independent of the temperature. But since $\frac{d\mathfrak{U}}{dp}$ is constant at constant temperature, $RT \frac{d\mathfrak{U}}{dp}$ is also independent of the volume. This quantity, therefore, is constant under all conditions to which the system is subjected. Let us write, $-RT \frac{d\mathfrak{U}}{dp} = a$, and we obtain,

$$p = \frac{RT}{v - f(v)} - \frac{a}{v^2}. \quad (28)$$

This equation, which is identical with the familiar formula that van der Waals has developed from purely kinetic considerations, is here shown to be directly deducible from a general thermodynamic equation, with the aid of two simple empirical observations, namely, the constancy of the specific heat of gases at constant temperature, and the proportionality between the cooling effect and the fall in pressure in the free expansion of gases.

Equation (28) does not define the nature of $f(v)$, and in this respect is less explicit than the corresponding term in the equation of van der Waals, which is a constant, b . Nevertheless it must be borne in mind that b , the volume correction in the formula of van der Waals, may only be regarded as constant when the volume is large, and that it also is in reality an undetermined function of the volume.

The constancy of the quantity, $R T \frac{d\alpha}{dp}$ or α , we have only proved in the cases of the gases which were experimented upon by Joule and Thomson, and through limited range of pressure. However, since the constancy of this term was established for all the gases tried, we may assume that the same result would have been obtained with any other gases through the same limits of pressure. It cannot be taken for granted that this constancy will hold at all pressures. In fact, the interpretation given by van der Waals for the quantity α , as the intermolecular attraction, would lead to the idea that it must be a function of the volume. Otherwise the attraction between two molecules would be independent of their distance apart. The variation of α with the volume will be mentioned later.

Van der Waals considered *a priori* that α would not depend upon the temperature. But it is evident from page 14 that it is a constant only if $\frac{dc_v}{dv} = 0$. Although the change of specific heat with moderate change of volume is negligible, the change through wide limits of volume is probably always a measurable quantity, as will be shown later.

Since the quantity α has been defined as equal to $-R T \frac{d\alpha}{dp}$, we should be able to determine its value from the data of Joule and Thomson. A calculation which is in effect the same as this has already been made by van der Waals,* who calculated from the values of a and b , given by experiment, the cooling effect that should be observed in free expansion. This cooling effect, in Centigrade degrees, for a change of one atmosphere in pressure is given below, as calculated by van der Waals and as determined by the averages of Joule and Thomson's results:—

	Temp. Cels.	Calculated.	Observed.
Air	17	0.265	0.259
"	90	0.18	0.206
CO ₂	18	0.9	1.15
"	91.5	0.64	0.703

The agreement, although not close, is very satisfactory considering the uncertainty of the experimental results.

2. *Liquids*.—The experimental proof of the continuity between the liquid and gaseous states shows that we must regard them as identical,

* *Kontinuität der F. und G. Zustand*, p. 116.

and any formula that is universally applicable to one state must also be applicable to the other. Thus all the equations already developed for gases apply without change to simple liquids (having a constant molecular weight) under the restrictions already mentioned, namely, that in the equations

$$p = \frac{RT}{v - f(v)} - \frac{d\mathfrak{U}}{dv} \quad \text{and} \quad p = \frac{RT}{v - b} - \frac{a}{v^2},$$

$\frac{d\mathfrak{U}}{dv}$ and $\frac{a}{v^2}$ are independent of the temperature only when $\frac{dc_v}{dv} = 0$, that a has not been proved to be a constant in all cases but may be a function of the volume, and that b is not necessarily a constant with changing volume, although it is in all cases independent of the temperature.

Regarding the question of the variability of c_v with the volume in the case of liquids we have no direct experimental evidence, but indirectly it can be shown that c_v is practically constant, for Ramsay and Young (page 14) found that equation (25), $p = AT - B$, applies to liquids as well as to gases, and this equation can only be true when $\frac{dc_v}{dv} = 0$.*

If $\frac{dc_v}{dv}$ is not equal to zero, then the general equation (8) must be used,

$$p = \frac{RT}{v} - T \frac{d\mathfrak{H}}{dv} - \frac{d\mathfrak{U}}{dv} + T \int_{T_0}^T \frac{1}{T} \frac{dc_v}{dv} dT;$$

this, differentiated with respect to T , v constant, gives

$$\frac{dp}{dT} = \frac{R}{v} - \frac{d\mathfrak{H}}{dv} - \frac{d^2\mathfrak{U}}{dv dT} + \int_{T_0}^T \frac{1}{T} \frac{dc_v}{dv} dT + \frac{dc_v}{dv}.$$

Since $\frac{d^2\mathfrak{U}}{dv dT} = \frac{dc_v}{dv}$ from equation (9),

$$\frac{dp}{dT} = \frac{R}{v} - \frac{d\mathfrak{H}}{dv} + \int_{T_0}^T \frac{1}{T} \frac{dc_v}{dv} dT = C + \int_{T_0}^T \frac{dc_v}{dv} \frac{dT}{T}, \quad (29)$$

where C is a constant; while from equation (25) $\frac{dp}{dT} = A$.

Notwithstanding this evidence for the approximate constancy of the specific heat, the experimental work of Joly † on this subject seems to

* Compare Nernst, Theor. Chem., p. 202.

† Phil. Trans. Roy. Soc., 182A, 73; Proc. Roy. Soc., XLVII. 218; LV. 390.

show that the value of c_v in a gas does change considerably through wide limits of volume. He has been the first to succeed in measuring directly the specific heat of gases at constant volume. The values were determined by means of his differential steam calorimeter, a method which seems to give very accurate and consistent results. The results showed that the specific heat at constant volume could be expressed in the following formulæ,

$$\text{For Air, } c_v = .17151 + .02788 \rho,$$

$$\text{For CO}_2, c_v = .1650 + .2125 \rho + .3400 \rho^2,$$

where ρ is the density in grams per cubic centimeter. According to these formulæ the specific heat at constant volume at atmospheric pressure differs from that at infinite volume by only two hundredths of one per cent in the case of air, and by three tenths of one per cent in the case of carbon dioxide. Between the specific heats of the gases at atmospheric pressure and in a highly compressed or liquid condition the change is much greater. For example, the value given by the formula for c_v in the case of carbon dioxide is about twice as great at the critical volume and about three and one half times as great in the liquid at 0°C . as the value for the gas at ordinary pressure. Further evidence of the change of c_v between the liquid and gaseous condition will be given later.

In these variations in the specific heat we find the probable cause of many of the deviations from the equation of van der Waals that have been noticed. It may be found necessary, therefore, in order to obtain a more exact equation of condition, to return to the more general equation (8),

$$p = \frac{R T}{v} + T \int_{T_0}^T \frac{1}{T} \frac{d c_v}{d v} d T - T \frac{d \mathfrak{H}}{d v} - \frac{d \mathfrak{A}}{d v},$$

in which the value of $\frac{d \mathfrak{H}}{d v}$ contains not only the function for volume correction, but also a term depending upon the value chosen for the lower limit of integration, T_0 . If we write

$$\frac{d \mathfrak{H}}{d v} = F(v), \text{ then } \frac{R T}{v} - F(v) T = \frac{R}{v - f(v)} T - F'(v) T,$$

where $f(v)$ denotes the same function of v that has been used in equations (27) and (28), namely, the quantity b in the van der Waals formula, and $F'(v)$, another function of v . Now $\frac{d c_v}{d v}$ is practically independent of the temperature and the equation may be written

$$p = \frac{RT}{v - f(v)} - T \ln \frac{T}{T_0} \frac{dc_v}{dv} - F'(v) T - \frac{d\mathfrak{A}}{dv}.$$

It is probable from the derivation of $F'(v)$ that this is a function of the same general nature as the preceding term, and will vary with the volume in the same way that $\frac{dc_v}{dv}$ does. Then, since the coefficient of $\frac{dc_v}{dv}$ is not a volume function, we may write, not as a complete expression, but as an approximation one step nearer the truth than the equations previously obtained, the following isothermal equation of condition,

$$p = \frac{RT}{v - f(v)} - \frac{d\mathfrak{A}}{dv} + c \frac{dc_v}{dv}, \quad (30 a)$$

or, after the type of the van der Waals equation,

$$p = \frac{RT}{v - b} - \frac{a}{v^2} + c \frac{dc_v}{dv}, \quad (30 b)$$

where c is a third constant to be determined by experiment, and which differs with different temperatures.

Equation (29) gives the corresponding equation isochore, which may be written for moderate ranges of temperature,

$$\frac{dp}{dT} = C - \frac{dc_v}{dv} \ln T. \quad (31)$$

These equations, (30) and (31), should furnish a more exact statement of the behavior of gases and liquids than the equation of van der Waals or the corresponding ones developed in this paper. Since the degree of accuracy is not known in the values of $\frac{dc_v}{dv}$ at present determined, I have not yet attempted an application of these equations.

Returning to the consideration of $f(v)$ or b , it may be stated at once that this quantity is always a function of the volume and decreases with decreasing volume, for usually the total volume in the liquid state is less than b calculated for the gaseous state, and if b were constant then $v - b$ would have a negative value, which would be meaningless. $v - b$ must always have a positive value.

The way in which the quantity a varies with the volume cannot be predicted. If it represents the attraction between the molecules, then it will vary inversely with the volume if the attraction between the molecules varies inversely with the distance. But since the attraction observed is probably the resultant of forces attractive and repulsive acting between

the molecules, we cannot say *a priori* how it will change with the distance between the molecules. In fact it is not necessary to suppose that a or $\frac{d\mathfrak{U}}{dv}$ must always have a positive value. Joule and Thomson found in the case of hydrogen a rise of temperature instead of the usual cooling effect on free expansion. This would indicate a small negative value of a , corresponding to a preponderance of repulsive force between the molecules. The unreliability of the experimental data, however, precludes certainty on this point.

In place of the equation

$$p = \frac{RT}{v - f(v)} - \frac{d\mathfrak{U}}{dv}, \quad p = \frac{RT}{v - b} - \frac{a}{v^2},$$

the equation of van der Waals, can be applied to liquids with the understanding that a and b are not constants but volume functions to be determined. In all liquids p is small compared with the other two terms. When $p = 0$, if we represent the volume by v_0 ,

$$\frac{RT}{v_0 - b} = \frac{a}{v_0^2}; \quad (32)$$

but since the volume of liquids is only slightly changed by changing the external pressure, $v_0 - b$ will not differ materially from $v - b$ at atmospheric pressure. We may write, then, as the equation for liquids at atmospheric pressure,

$$\frac{RT}{v - b} = \frac{a}{v^2}. \quad (33)$$

From this equation may be found the values of a and b when the volume of a liquid is known at two different temperatures. From the values thus found it should be theoretically possible to calculate the compressibility of the liquid at constant temperature. Thus by differentiating the van der Waals equation we obtain the reciprocal of the compressibility,

$$\frac{dp}{dv} = -\frac{RT}{(v - b)^2} + 2\frac{a}{v^3};$$

practically this method fails on account of the fact that the difference between the last two terms is very small compared with their total values, and therefore any error in either of these terms is multiplied enormously in the determination of $\frac{dp}{dv}$.

The values of a and b obtained from equation (33) will be of service

later in discussing certain relations between the liquid and gaseous state. The way in which a and b change with varying conditions of a liquid is illustrated by the following values, calculated for fluor-benzol, from the data given by Young.* For the values at high pressures p is not negligible compared with $\frac{a}{v^2}$, equation (33) will not give exact results, and recourse must be had to the original equation of van der Waals. v represents molecular volume in litres, p is expressed in atmospheres, and b and a in units corresponding.

v	b	a
.097	.00075	11.6
.111	.00078	12.8
.127	.00081	13.5
.157	.00088	15.0
.225	.00110	17.9
.232	.00114	18.2

By extrapolation from these values we find for $v = .270$ the

critical volume.270 .00126 19.7

From the critical data a and b are

determined to be270 .00128 19.9

It is evident that the values of a and b obtained from the data for the thermal expansion of a liquid are entirely consistent with those determined from the critical data. The change of b with the volume is well shown by the figures, and is typical. Regarding the variation in a , however, it is not possible to say whether it is due to change in volume or change in temperature, or both.

It must be emphasized that in all the preceding work on gases and liquids we are dealing with substances composed of a single molecular species. Gases and liquids in which dissociation or association occur are not within the scope of this section.

(B.) *Heterogeneous Systems.*

1. *Gases and Liquids.* — The simplest case of heterogeneous equilibrium in a system composed of a single molecular species is that between a simple liquid and its vapor. We may apply to this case the general equation of equilibrium (11 a). If we consider the specific heat at con-

* Phil. Mag., XXXIII. 153.

stant volume the same in the liquid and its vapor, the equation assumes the simpler form

$$R T \ln \frac{v_2}{v_1} = P V - U - H T, \quad (34)$$

where v_1 and v_2 represent the molecular volumes in the liquid and gaseous states respectively. From the previous section we know that the term H will enter simply as a volume correction. The exact manner in which it so enters may be best shown by finding the free energy of the process of liquefaction from the work that might be done if the vapor were compressed isothermally and continuously until it reached the liquid condition. This work would be equal to $\int p dv$, and p can be found in terms of v from the equation of condition which holds good throughout the process. From equation (27)

$$p = \frac{R T}{v - f(v)} - \frac{d\mathfrak{A}}{dv}.$$

Therefore

$$A = \int_{v_2}^{v_1} p dv = \int_{v_2}^{v_1} \frac{R T}{v - f(v)} dv - \int_{v_2}^{v_1} d\mathfrak{A}.$$

The integration of $\frac{R T}{v - f(v)} dv$ is only possible when the form of $f(v)$ is known; but since $f(v)$ does not change greatly, and since it is only an important part of the expression when v is small, it may be regarded as a constant, and equal to the value of $f(v)$ in the liquid state, or b_1 . This value may be found from equation (33). Then the above equation becomes

$$A = R T \ln \frac{v_2 - b_1}{v_1 - b_1} + U,$$

and for equilibrium from equation (11), $A = P V$.

$$R T \ln \frac{v_2 - b_1}{v_1 - b_1} = P V - U. \quad (35)$$

Since b_1 is but small compared with v_2 , we may replace $v_2 - b_1$ by v_2 . Since U represents the change of internal energy in vaporization, and $P V$ the external work, $-U + P V$ will be equal to the ordinary heat of vaporization per gram-molecule, including the external work. This whole quantity may be designated by L . Then

$$R T \ln \frac{v_2}{v_1 - b_1} = L. \quad (36)$$

This equation of equilibrium, which is at the same time a simple formula for the heat of vaporization, has been deduced for all cases in which there is no change in the molecular weight or in the specific heat at constant volume during vaporization. Let us, in the following table, compare for a few substances the experimentally determined values of L with those calculated from equation (36).

R is in such units that L will be in gram-calories, and equals 1.98. The values of b_1 are obtained from the coefficient of thermal expansion of the liquid by equation (33). For the value of v_2 , the molecular volume of the vapor, in the cases in which they have not been experimentally determined, I have used the volume which a gram-molecule of a perfect gas would have under the same conditions. The error thus introduced will be negligible, for a large error in v_2 or in $v_1 - b_1$ will affect only slightly the value of L .

	Temp. C.	v_1	b_1	v_2	L (calc.)	L (obs.)
Ether	35	.1062 *	.080	24.82	4,200	6,600 §
Benzol	80	.096 †	.065	28.87	4,800	7,200
Methyl formiate .	40	.0627 ‡	.047	25.02 ‡	4,500	6,900 ¶
Methyl propionate	80	.1047 ‡	.077	27.50 ‡	4,800	7,400 **

The results are very interesting, the calculated values being in each case about two thirds of the observed. The explanation of the lack of agreement must lie in the failure of the substances to comply with the conditions named above. We have no reason to suspect, in the case of all these substances, the polymerization of the molecules in the liquid state. We are therefore again led to the belief that the specific heat at constant volume is, in general, different in the liquid and gaseous states. Moreover, I think that it is possible to show this in another, entirely independent way. The specific heat at constant pressure of a substance is the sum of two quantities, one representing the internal change in energy and the other the external, that is,

$$c_p = \left(\frac{dU}{dT} \right)_p + P \left(\frac{dv}{dT} \right)_p, \quad (37)$$

* Kopp: Jahresber. der Chem., 1860.

† Pisati, Paterno: Jahresber., 1874.

‡ Young, Thomas: Phil. Mag., XXXIV. 508.

§ Brix: Pogg. Ann., LV. 341.

|| Wirtz: Wied. Ann., XL. 438.

¶ For 32.9°, Andrews: Pogg. Ann., LXXV. 501.

** Schiff: Lieb. Ann., CCXXXIV. 338.

where $\left(\frac{d\mathfrak{U}}{dT}\right)_P$ and $\left(\frac{dv}{dT}\right)_P$ represent the change of internal energy and volume respectively, with a change of temperature at constant pressure, P .

$$\left(\frac{d\mathfrak{U}}{dT}\right)_P = \left(\frac{d\mathfrak{U}}{dT}\right)_v + \left(\frac{d\mathfrak{U}}{dv}\right)_T \left(\frac{dv}{dT}\right)_P,$$

$$\left(\frac{d\mathfrak{U}}{dT}\right)_v = c_v,$$

$$c_v = \left(\frac{d\mathfrak{U}}{dT}\right)_P - \left(\frac{d\mathfrak{U}}{dv}\right)_T \left(\frac{dv}{dT}\right)_P;$$

from (37),

$$\left(\frac{d\mathfrak{U}}{dT}\right)_P = c_P - P \left(\frac{dv}{dT}\right)_P,$$

$$c_v = c_P - \left(\frac{dv}{dT}\right)_P \left(\frac{d\mathfrak{U}}{dv}\right)_T - P \left(\frac{dv}{dT}\right)_P,$$

$$c_v = c_P - \left(\frac{dv}{dT}\right)_P \left[P + \left(\frac{d\mathfrak{U}}{dv}\right)_T \right]. \quad (38)$$

We have found for a gas or a liquid, $\frac{d\mathfrak{U}}{dv} = \frac{a}{v^2}$. Substituting in (38),

$$c_v = c_P - \left(\frac{dv}{dT}\right)_P \left(P + \frac{a}{v^2} \right). \quad (39)$$

Since $\left(\frac{dv}{dT}\right)_P$ is the measure of thermal expansion, equation (39) contains only quantities capable of experimental determination, and we are able to calculate c_v from the experimentally found value of c_P . The calculation is further simplified by the fact that in the case of most vapors $\frac{a}{v^2}$ is negligible compared with P , and in liquids P is negligible compared with $\frac{a}{v^2}$. For close approximations, therefore, we may write for liquids,

$$c_v = c_P - \frac{a}{v^2} \left(\frac{dv}{dT}\right)_P; \quad (40a)$$

and for vapors,

$$c_v = c_P - P \left(\frac{dv}{dT}\right)_P = c_P - R, \quad (40b)$$

that is, the equation for the specific heats of perfect gases applies to

vapors in which $\frac{a}{v^2}$ is negligible compared with the atmospheric pressure.

The molecular specific heats at constant pressure of ether in the liquid and gaseous states are 40.48 and 31.67 respectively. At 30 degrees, the coefficient of thermal expansion for the liquid is .000163; $v = .1054$ litres; a , calculated by means of equation (33), in such units that $\frac{a}{v^2}$ is in atmospheres, is equal to 10.84. From these data $\frac{a}{v^2} \left(\frac{dv}{dT} \right)_P = .1590$ in litre-atmospheres, or 3.843 in gram-calories. Subtracting the latter value from 40.48, we obtain 36.64 as the molecular specific heat at constant volume of liquid ether. From the value 31.67, subtracting the value of R , 1.98, we obtain 29.69 as the molecular specific heat at constant volume of ether vapor. The difference between these values is far greater than could be explained by experimental errors.

It is interesting to see whether an explanation of such variations in specific heat at constant volume can be found from the kinetic point of view. We must believe that the energy imparted to a substance for an increase in the progressive motion of its molecules corresponding to a definite rise in temperature must be independent of the conditions of the substance. If, however, the heat energy of a body is due not only to the progressive motion of its molecules, but also to some additional motion such as the vibration or rotation of molecules, then the energy given to the body in raising its temperature would be in part used in increasing the progressive motion and in part in increasing the secondary motions of vibration, rotation, etc. The quantity of energy required for the latter would not necessarily be independent of the volume of the body, but might depend upon the proximity or rate of collision of the molecules. If, however, a body were composed of molecules incapable of any except progressive motion, we should predict absolute constancy in the specific heat at constant volume. Mercury vapor is believed to be such a body, and if liquid mercury, as seems probable, also is composed of monatomic molecules, the value of c_v in the two states should be identical. Unfortunately the specific heat of mercury vapor is unknown, and we cannot test the correctness of this supposition directly. But if it be true, equation (36) should give a correct result for the heat of vaporization of mercury. A calculation similar to those whose results appear on page 23 gives, for $T = 623$, $v_1 = .01566$, $b_1 = .01419$, $v_2 = 58.7$, $L = 13,070$. The value experimentally observed by Person (1846) was 12,400.*

* Comptes Rendus, XXIII. 162 *et seq.*

The agreement is satisfactory and within the limits of experimental error.

2. *The Vapor Pressure Curve.*—The change with changing temperature of the equilibrium between a vapor and its liquid or solid phase may be obtained from equation (20); for if we consider the vapor to obey with sufficient exactness the laws of perfect gases, the system under consideration is one for which equation (20) was developed, since it contains only a gaseous phase and a condensed phase of definite composition.

$$\text{From equation (20),} \quad \frac{d \ln K}{dT} = \frac{U}{R T^2}.$$

$$\ln K = \ln v - \ln v',$$

where v is the molecular volume of the vapor, v' that of the solid or liquid. $\frac{d \ln v'}{dT}$ is entirely negligible compared with $\frac{d \ln v}{dT}$, and equation (20) becomes

$$\frac{d \ln v}{dT} = \frac{U}{R T^2}.$$

Since $v = \frac{R T}{p}$, where p is the vapor pressure,

$$\ln v = -\ln p + \ln R + \ln T,$$

$$\text{and} \quad d \ln v = -d \ln p + \frac{1}{T} dT.$$

$$\text{Substituting,} \quad \frac{d \ln p}{dT} = -\frac{U}{R T^2} + \frac{1}{T} = \frac{-U + R T}{R T^2}.$$

As on page 22, let $-U + R T = L$,

$$\text{then} \quad \frac{d \ln p}{dT} = \frac{L}{R T^2},$$

which is the familiar expression for the vapor pressure curve.

A complete expression for the vapor pressure in the case of liquids to which equation (36) applies, if the vapor approximates a perfect gas, may be derived as follows:

$$\ln \frac{v}{v' - b'} = \frac{L}{R T}.$$

Substitute $\frac{R T}{p}$ for v , and

$$\ln \frac{R T}{p(v' - b')} = \frac{L}{R T}, \quad \text{or} \quad \frac{R T}{p(v' - b')} = e^{\left(\frac{L}{R T}\right)},$$

whence

$$p = \frac{R T}{(v' - b') e^{\left(\frac{L}{R T}\right)}}$$

III. DIMOLECULAR SYSTEMS.

Solutions. — The simplest case of a system composed of two molecular species is one in which the two species are chemically neutral, only acting on each other by the process of solution.

Before taking up such systems it will be convenient to consider briefly, in the light of the results of the last section, a question concerning the general equation of equilibrium, namely, the nature of the function H . In equation (5), which expresses the free energy of a simple constituent of a system, the quantity \mathfrak{H}_1 entered as an integration constant, and nothing was known regarding its nature except that it must be independent of the temperature. After differentiating equation (5), it was found

that $\frac{d\mathfrak{H}_1}{dv_1}$ was a function which could represent in the later equations the volume correction corresponding to the quantity b in the equation of van der Waals. Since this was true in the widely differing states of gas and liquid, it is probable that in any state in which the molecule itself is not changed $\frac{d\mathfrak{H}_1}{dv_1}$ may be expressed as such a volume correction, rep-

resenting the diminution of the space available for the free motion of the molecules, due to the space actually occupied by the molecules themselves. If, therefore, we subtract from \mathfrak{H}_1 the term representing the volume correction, there will remain a quantity which will be constant under all conditions when the molecule itself does not change, and whose value will depend only on the nature of the substance considered. We will use \mathfrak{h} hereafter to denote this quantity. The volume correction enters in the most general way in the consideration of a phase containing a number of molecular species. When we consider each species, the volume must be corrected for the volume actually occupied by its own molecules and also for that occupied by the other molecules present. The volume with the first correction may be expressed as in the van der Waals equation by $v - b$, where b is the correction due to the space occupied by its own molecules. The volume may be corrected for the space occupied by the other kinds of molecules by multiplying the actual volume by a factor, r , representing the fraction of any volume of the mixture which is left available for the free motion of the molecules of the particular species under consideration. The nature of this species should have no effect on the quantity r . We have, therefore, for the corrected volume of a substance dissolved in any mixture the value $r(v - b)$, where r depends solely on the nature of the solvent, b on that of the solute.

In taking up the subject of solutions it will be necessary to consider their probable nature. Although there is some evidence that the phenomenon of solution is accompanied by a molecular change, the preponderance of evidence seems to be in favor of the theory that the molecule of a substance in solution is free, and not combined in any chemical way with the molecules of the solvent. If this is the case, certain properties of the solute should remain unchanged regardless of the nature of the solvent. In the following work we will assume that, for a dissolved substance, the quantity h as defined above and the quantity c_v will be the same in any solvent. If this supposition, which seems eminently probable, proves to be not entirely correct, then the equations developed below will only be approximations to the truth. It is to be hoped that in any case their application will conversely give us information concerning the nature of solution.

Osmotic Pressure.—The simplest phenomenon of a homogeneous solution is that of osmotic pressure, which may be determined in the following way. The change of free energy on addition of an infinitesimal amount of solvent to a solution containing one gram-molecule of solute is equal to the sum of the changes of free energy in the two constituents of the system. From equation (5), if $\frac{dc_v}{dv} = 0$, and $\frac{d\mathfrak{H}}{dv}$ becomes the volume correction, which, as is shown by Nernst,* is for each constituent, in the case of osmotic pressure, only the correction for the space occupied by the molecules of the constituent in question,

$$dA = \frac{RT}{v_1 - b_1} dv_1 - d\mathfrak{U}_1 + \frac{nRT}{v_2 - b_2} dv_2 - d\mathfrak{U}_2,$$

where the subscript 1 refers to the solute, subscript 2 to the solvent. dv_1 , the change in molecular volume of the solute, is also the change in volume of the system, and $dA = p dv_1$, where p is the osmotic pressure. Therefore

$$p = \frac{RT}{v_1 - b_1} - \frac{d\mathfrak{U}}{dv_1} + \frac{nRT}{v_2 - b_2} \frac{dv_2}{dv_1}, \quad (41)$$

where $\frac{d\mathfrak{U}}{dv_1}$ represents the heat produced by the addition of dv_1 of the solvent. Except in cases of solution of such great concentration that the molecular volume of the solute and that of the solvent are not greatly different, $\frac{dv_2}{dv_1}$ is entirely negligible, and the equation for osmotic pressure becomes

* Theor. Chem., p. 209. (References to this book are to the first edition.)

$$p = \frac{RT}{v-b} + \frac{d\mathfrak{U}}{dv}. \quad (42)$$

Except that $\frac{d\mathfrak{U}}{dv}$ represents the heat of dilution instead of the heat of free expansion, equation (42) is identical with the equation obtained for gases. The comparison of this formula with experiment is not possible with the experimental data at present available, since, as far as I know, the heat of dilution has been determined only in the case of electrolytes, and in these cases a complication is introduced, due to the heat of dissociation. An abstract* has just come to hand of a recent work by Kistiakowski,† in which he shows that the lowering of the freezing point, which is proportional to the osmotic pressure, is, in a concentrated solution, equal to the lowering calculated for an ideal solution plus a term that is proportional to the heat of dilution. This is the result that would be given by equation (42). Kistiakowski shows that there is perfect agreement between the lowering of the freezing point calculated in this way and that found by experiment. It seems questionable, however, whether his application of the formula to electrolytes, neglecting the heat of dissociation, is justifiable. Unfortunately I have not access to his original paper.

The osmotic work obtainable from the change of a gram-molecule of a solute from a solution of one concentration to one of another concentration may be found by direct application of equation (6), or by integration of $p dv$, where p may be expressed in terms of v by means of equation (42). Then

$$A = RT \ln \frac{v_2 - b}{v_1 - b} + U. \quad (43)$$

For all except very concentrated solutions b may be neglected, and

$$A = RT \ln \frac{v_2}{v_1} + U. \quad (43a)$$

Cady‡ has recently shown that in a galvanic cell in which the total result of the current is the passage of a certain amount of a metal from an amalgam of one concentration to one of another,

$$\pi = \frac{RT}{n e_0} \ln \frac{v_2}{v_1} + q,$$

* Chem. Centr. Blat., 1899, I. 89.

† Jour. Russ. Phys. Chem. Ges., XXX. 576.

‡ Jour. of Phys. Chem., II. 551, 1898.

where π is the electromotive force, v_1 and v_2 are the molecular volumes of the metal in the two amalgams, and q is the heat of the process in electrical units. From this,

$$n e_0 \pi = R T \ln \frac{v_2}{v_1} + U,$$

but $n e_0 \pi$ is the electrical work per gram-molecule, which is equal to the change of free energy, since the cell is a reversible one. Therefore $A = n e_0 \pi$, or

$$A = R T \ln \frac{v_2}{v_1} + U,$$

which is identical with (43 a).

When we consider solutions of all concentrations, varying from the state where one of the constituents of the phase is in great excess to the state where the other constituent is in great excess, as, for example, when water is added continuously to a definite amount of alcohol, then the form which the osmotic pressure curve assumes is very complicated.

Here equation (41) must be used, and $\frac{dv_2}{dv_1}$ and $\frac{d\mathfrak{U}}{dv_1}$ will both be com-

plex functions of v_1 . $\frac{d\mathfrak{U}}{dv_1}$ may be looked upon as the sum of two quanti-

ties, one due to the attraction of unlike, the other to the attraction of like molecules. Concerning the manner in which the former will change we are ignorant. The latter, however, according to reasoning exactly

similar to that which led van der Waals to the term $\frac{a}{v_2}$, may be shown to be inversely proportional to the square of the volume, or equal

to $\frac{a_1 + a_2}{v^2}$. We see from this that equation (41) is at least of the

third degree in v_1 . Bredig* and Noyes† have each proposed a general formula for osmotic pressure based upon kinetic reasoning. Both these equations are of the third degree in v . The osmotic pressure curve represented by equation (41) is not necessarily, therefore, single valued. There may be more than one volume corresponding to one osmotic pressure. This is a further analogy between solutions and gases. In fact, a number of cases are known in which the osmotic pressure may be shown to be the same at two different concentrations, namely, the cases of liquids that are mutually soluble to a limited extent, thus forming two phases in equilibrium with each other. It is evident that in order to

* Zeit. Phys. Chem., IV. 444.

† Zeit. Phys. Chem., V. 53.

preserve the equilibrium the osmotic pressure, not only of one but of each of the constituents, must be the same in the two phases. No similar phenomena have ever been observed in the case of solids dissolved in liquids, but it seems not impossible that such may be found. Then a solid might have two different solubilities in a solvent at one temperature, corresponding to two concentrations in which the osmotic pressure would be equal to the solution pressure.

Distribution of a Solute between two Solvents. — The equation of equilibrium when a substance is distributed between two solvents may be found directly from equation (11 a), simplified by the considerations advanced on page 27, namely,

$$P V = R T \ln \frac{r_2 (v_2 - b)}{r_1 (v_1 - b)} + U. \quad (44)$$

In all cases of this sort $P V$ is entirely negligible, and

$$R T \ln \frac{r_2 (v_2 - b)}{r_1 (v_1 - b)} + U = 0, \quad (45)$$

where v_2 and v_1 are the molecular volumes of the solute in the two solvents; b is the volume correction for the solute molecules; r_1 is the volume correction for the first solvent, and r_2 that for the second. U is the heat given off when one gram-molecule of the solute passes from one solvent to the other. It equals the difference between the heats of solution of the solute in the two solvents. In all ordinary solutions b is negligible, and the equation becomes

$$R T \ln \frac{r_2 v_2}{r_1 v_1} + U = 0. \quad (46)$$

Since this is the general equation of distribution of a substance between two solvents, it will hold true in the special case in which the solutions are in equilibrium with the solute in the solid form. If we represent by s_1 and s_2 the solubilities in gram-molecules of the solute in one litre of each of two solvents, then $s_1 = \frac{1}{v_1}$ and $s_2 = \frac{1}{v_2}$, and equation (44) may be written

$$R T \ln \frac{r_2 s_1}{r_1 s_2} + U = 0; \quad (47)$$

or if U' is the heat of solution in the first solvent, U'' in the second,

$$R T \ln \frac{r_2 s_1}{r_1 s_2} + U' - U'' = 0,$$

$$\text{or} \quad RT \ln \frac{s_1}{r_1} + U' = RT \ln \frac{s_2}{r_2} + U''. \quad (48)$$

This equation permits the calculation of the solubility of a substance in any solvent if the solubility in any other solvent is known and the heat of solution in each solvent, or the difference between these heats of solution, and if the ratio of the volume corrections for the two solvents is known.

The heat of solution may be found from the change of solubility with change of temperature by the well known equation

$$\frac{d \ln s}{dT} = \frac{U}{RT^2}, \quad (49)$$

which may be obtained by direct application of equation (20), since the conditions for which (20) was obtained are all fulfilled in this case, and since the molecular volume, v_0 , of the solid may be considered constant.

$$K = v_0 s; \quad \ln K = \ln v_0 + \ln s; \quad d \ln K = d \ln s.$$

Uniting equations (48) and (49),

$$RT \ln \frac{s_1}{r_1} + RT^2 \frac{d \ln s_1}{dT} = RT \ln \frac{s_2}{r_2} + RT^2 \frac{d \ln s_2}{dT},$$

$$\text{or} \quad \ln \frac{s_1}{s_2} + T \frac{d \ln \frac{s_1}{s_2}}{dT} - \ln \frac{r_1}{r_2} = 0. \quad (50)$$

When the values of r are known for the various solvents, if we know the solubility of a substance in two solvents and the temperature coefficient of the solubility in one, we may find the corresponding coefficient in the other solvent. I hope soon to verify these formulæ experimentally, and to determine the values of r for some common solvents. It will be interesting to see how r compares with the value of $v - b$ found for the solvents by equation (33).

IV. POLYMOLECULAR SYSTEMS.

(A.) *Homogeneous Systems.*

In accordance with the considerations advanced on page 27, the general equation of equilibrium (11 a) may be put into the form

$$PV = RT \ln \frac{[r(v_2 - b_2)]^{n_2} [r(v'_2 - b'_2)]^{n'_2} \dots}{[r(v_1 - b_1)]^{n_1} \dots} - T \int_{T_0}^T \frac{C_{v_1} - C_{v_2}}{T} dT + hT + U,$$

where h is the sum of all the $\frac{h}{T}$ terms, and $(C_{v1} - C_{v2})$ and h have the same value regardless of the nature of the solvent. If the total change in the number of molecules be n , then the quantity r will occur to the power of n , and

$$P\bar{V} = RT \ln r^n \frac{(v_2 - b_2)^{n_2} (v'_2 - b'_2)^{n'_2} \dots}{(v_1 - b_1)^{n_1} \dots} - T \int_{T_0}^T \frac{C_{v1} - C_{v2}}{T} dT + hT + U. \quad (51)$$

Only in the case of equilibrium between gases is $P\bar{V}$ considerable, for other cases $P\bar{V}$ may be neglected. For equilibrium in liquid phases, if we represent by k the equilibrium ratio with the volume corrections

$$b_1, b_2 \text{ etc., and represent } h - \int_{T_0}^T \frac{C_{v1} - C_{v2}}{T} dT \text{ by } f,$$

$$\text{then} \quad (RT \ln r^n k) + U + fT = 0, \quad (52)$$

$$\text{or} \quad (RT \ln k) = -RT \ln r^n - U - fT. \quad (52a)$$

We are now in a position to answer the question how equilibrium is influenced by the nature of the solvent. If we write for equilibrium in two solvents two equations of the form of (52a),

$$(RT \ln k) = -RT \ln r^n - U' - fT,$$

$$(RT \ln k') = -RT \ln r'^n - U'' - fT,$$

and subtract, we obtain, since f is the same in the two solvents, according to the assumption made on page 28,

$$\ln \frac{k'}{k} = -n \ln \frac{r'}{r} - \left(\frac{U' - U''}{RT} \right), \quad (53)$$

and we find that the condition of equilibrium depends on the values of r and the heat of the reaction in the two solvents. Ordinarily when the solvent does not enter into the reaction, the values of $(v_1 - b_1)$, etc. may be replaced by v_1 , etc., and k , the corrected equilibrium ratio, may then be replaced by K , the ordinary equilibrium ratio. If we are dealing with reactions in which the original and final number of molecules is the same, or with any case where $n \ln \frac{r'}{r}$ is negligible, the equation becomes

$$\ln K' - \ln K'' = \frac{U'' - U'}{RT}. \quad (54)$$

In such cases the difference between the logarithms of the equilibrium ratios in any two solvents at a given temperature is equal to the difference in the heats of the reaction divided by the gas constant and by the absolute temperature. I know of no case in which the experimental

data are at present sufficiently complete to permit the testing of equation (54).

V. APPLICATION TO ELECTRO-CHEMISTRY.

Since the electrical work of a reversible cell is equal to the change of free energy of the process taking place in the cell, the calculation of electromotive force in many cases is possible by means of the general equation (6).

The general formula for the electromotive force of a concentration cell has already been given on page 29.

Let us consider next the subject of a single potential difference between a metal and an electrolyte containing the ions of that metal. If \mathfrak{A}_1 be the free energy of one gram-molecule of the metal, and \mathfrak{A}_2 that of one gram-molecule of its ions, then the electrical work in the electrolytic solution of one gram-molecule is

$$A = \mathfrak{A}_1 - \mathfrak{A}_2.$$

Now for \mathfrak{A}_2 we obtain from equation (5), modified according to page 27,

$$\mathfrak{A}_2 = -R T \ln r (v_2 - b_2) - T \int_{T_0}^T \frac{c_{v_2}}{T} dT + h_2 T + \mathfrak{U}_2,$$

where r is the correction for the particular solvent in which the ions are dissolved, b_2 the correction for the ions themselves, which will always be negligible. c_{v_2} and h_2 are independent of the nature of the particular solvent. \mathfrak{U}_2 is the internal energy of the ions, and if we represent by \mathfrak{U}_1 the internal energy in the electrode, and by U the change of internal energy in electrolytic solution, $U = \mathfrak{U}_1 - \mathfrak{U}_2$, and $-\mathfrak{U}_2$ may be replaced by $U + \mathfrak{U}_1$. Then since \mathfrak{A}_1 , \mathfrak{U}_1 , c_{v_2} , h_2 , are constants at constant temperature,

$$A = C + (R T \ln r v_2) + U,$$

where C is a constant including the various terms mentioned above. If we replace v_2 by $\frac{RT}{p}$, where p is the osmotic pressure of the ions, we may write

$$A = C + (R T \ln R T) - R T \ln \frac{p}{r} + U = c - R T \ln \frac{p}{r} + U.$$

If for convenience we write $c = R T \ln P$,

$$A = -R T \ln \frac{1}{r} \frac{p}{P} + U,$$

or, since $A = \nu e_0 \pi$, where ν is the valence of the ion, e_0 the electricity carried by a gram-molecule of a univalent ion, and π the electromotive force, then

$$\pi = -\frac{RT}{\nu e_0} \ln \frac{1}{rP} + \frac{U}{\nu e_0}, \quad (55)$$

in which P differs from the electrolytic solution pressure of Nernst in that it is at constant temperature the same, no matter what the solvent may be in which the ions are dissolved, while the value of the Nernst solution pressure holds good only for water solutions. r represents the particular volume correction of the solvent.

An interesting type of cell is one in which two similar electrodes are in contact with solutions of an electrolyte containing the electrode ion in two different solvents; as, for example, zinc, zinc sulphate in water, zinc sulphate in alcohol, zinc. When a current passes through this cell, the total change consists in the transfer of zinc sulphate from one solvent to another. The free energy change in a cell of this type may be found from equation (6), modified as in equation (46),

$$A = RT \ln \frac{r_2^2 v_2 v_2'}{r_1^2 v_1 v_1'} + U, \quad (56)$$

where v_1 and v_1' are the molecular volumes of the positive and negative ions respectively, in the first solvent; v_2 and v_2' , in the second solvent. Now $v_1' = g v_1$, where g is a whole number or a simple fraction; also, $v_2' = g v_2$. Therefore,

$$A = RT \ln \frac{r_2^2 v_2^2}{r_1^2 v_1^2} + U = 2 RT \ln \frac{r_2 v_2}{r_1 v_1} + U. \quad (57)$$

If m represents the number of gram-molecules transferred from one solvent to the other when the quantity of electricity, νe_0 , passes through the cell, then

$$\nu e_0 \pi = 2 m RT \ln \frac{r_2 v_2}{r_1 v_1} + m U.$$

Let $m U = q$, then

$$\pi = \frac{2 m}{\nu e_0} RT \ln \frac{r_2 v_2}{r_1 v_1} + \frac{q}{\nu e_0}. \quad (58)$$

From the equation of Helmholtz,

$$\pi = \frac{d\pi}{dT} T + \frac{q}{\nu e_0}, \quad (59)$$

and comparing (58) and (59) it is evident that

$$\frac{d\pi}{dT} = \frac{2 m}{\nu e_0} R \ln \frac{r_2 v_2}{r_1 v_1}. \quad (60)$$

In an investigation which I am now making on cells of the above type I have attempted a verification of these equations in the following way. Choosing two solvents in which the value of $\ln \frac{r_2}{r_1}$ may be neglected, namely, water and a mixture of alcohol and water, then if v_2 be made equal to v_1 , $\frac{d\pi}{dT}$ should equal zero. Unfortunately the dissociation in alcohol-water mixtures of the salts that are available for our purpose has not hitherto been determined. If the two solutions are made up with equivalent amounts of the original salt, then the concentration of the ions in the alcohol-water solution will be less than that in the water solution on account of the greater dissociative power of water. In the following cells, made up in this way, we should expect, therefore, a small temperature coefficient, and moreover, since the electrode in contact with the water solution is found to be negative, this temperature coefficient should be negative.

The following table gives the results obtained for the cells:—
 (1) Zinc; zinc sulphate, tenth normal, in water and fifty per cent ethyl alcohol. (2) Zinc; zinc sulphate, tenth normal, in water and fifty per cent methyl alcohol. (3) Cadmium; cadmium sulphate, tenth normal, in water and sixty per cent ethyl alcohol. (4) Thallium; thallium sulphate, hundredth normal, in water and twenty-seven per cent ethyl alcohol. (5) Thallium; thallium sulphate, hundredth normal, in water and forty per cent methyl alcohol.

	Temp. C	π	$\frac{d\pi}{dT}$
(1)	30	.043	-.00013
	0	.047	
(2)	23	.0475	-.00002
	0	.0480	
(3)	28	.046	-.00011
	0	.049	
(4) A	23	.0212	.00000
	0	.0212	
B	24	.0216	-.00001
	0	.0218	
C	30	.0242	-.00001
	0	.0246	
(5)	24	.0380	.00000
	10	.0380	

In order to determine the actual dissociation in the above cases conductivity determinations were made. I found in the case of zinc and cadmium sulphates that the degree of the dissociation could not be found from conductivity determinations on account of peculiarities which will be discussed in a later paper. It was found, however, that in the case of cadmium sulphate the dissociation is at least five or six times as great in water as in fifty per cent methyl alcohol. In the first three cases, therefore, the value of $\frac{v_2}{v_1}$ is undoubtedly great enough to account for the values of $\frac{d\pi}{dT}$ found.

On the other hand, in the case of thallium sulphate it was found possible to determine the degree of dissociation from the conductivity data. In dilute solutions the dissociation in water and in fifty per cent methyl alcohol was found to be practically the same. This is in complete agreement with the result in case (5), where the temperature coefficient was zero. In case (5), then, the only one in which all the data are available, equation (60) is thoroughly verified. I hope to publish soon more complete results on this subject.

I wish to express my deep obligation to Professor Theodore W. Richards for his encouragement and friendly criticism of this work.

SUMMARY.

I. (a) A general equation for change of free energy is developed.

(b) From this is derived a general expression for physico-chemical equilibrium in homogeneous or heterogeneous systems, which includes as special cases the law of isothermal mass-action and the laws of constancy of distribution coefficients among several phases.

(c) For change of equilibrium with change of temperature a formula is derived of which the equation of van't Hoff is a specialized form.

II. (a) The application of the general equations to gases yields an equation of condition which with the aid of two familiar empirical observations is shown to be identical with the equation of van der Waals.

(b) This equation of condition is applied to liquids in detail and special cases are discussed.

(c) A more complete equation is proposed, recognizing the variability of specific heat with changing volume.

(d) From the general equation a formula is obtained for equilibrium

between a liquid and its vapor. Heats of vaporization are calculated from this formula.

(e) The formula is inapplicable in cases where the specific heat at constant volume differs in the liquid and gaseous state. A method of calculating these specific heats is given.

(f) The formula applies perfectly in the case of mercury.

(g) The vapor pressure curve is discussed.

III. (a) Application of the general equations to solutions leads to simple expressions for osmotic pressure and osmotic work in concentrated solutions.

(b) Equations are given for the distribution of a solute between two solvents, and for the relation between the solubility curves of a substance in different solvents.

IV. The influence of the nature of the solvent upon general homogeneous equilibrium is determined and formulas are given.

V. (a) The general equation for free energy is applied to electrochemistry. For the single potential difference between a metal and an electrolyte an equation is proposed which is an amplification of the equation of Nernst.

(b) Galvanic cells in which two solvents take part are discussed.

